STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. V. RAMAN EFFECT OF HOMO-CYCLIC COMPOUNDS.

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Introduction.

Of the Raman spectra of homo-cyclic compounds, several investigations have been carried out on the monocyclic compounds, such as benzene cyclohexane and their derivatives(1), but comparatively few papers on the condensed ring compounds have been published. Naphthalene and its halogen and alkyl substitution products have been studied by Ziemecki(2) and by Gockel(3), and some hydrogenated derivatives by Bonino and Cella(4), and by Mukerji(5). The experimental data of indene have been reported recently by Bonino and Ansidei(6). In the present investigation, the studies of the Raman spectra of benzene, cyclohexane, indene, naphthalene, tetrahydro-naphthalene, and decahydro-naphthalene have been repeated and the studies have been now extended to the condensed tri-cyclic and tetra-cyclic compounds, such as tetrahydro-acenaphthene, decahydro-acenaphthene, decahydro-pyrene and perhydro-pyrene, which have not been reported hitherto.

Experimental.

Most of the substances used were kindly supplied by Dr. Kageyama of the Fuel Research Institute of Navy in Tokuyama, excepting naphthalene and indene. Commercial pure naphthalene (Merck's) was repurified by means of recrystallization (from alcohol) and sublimation. The alcohol solution (4/100 mol) and benzene solution (ca. 5/100 mol) of naphthalene were used in the experiments of the Raman spectra. As to indene, the chemically pure substance, made by Takeda, was fractionated over metallic sodium.

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(1) Kohlrausch, "Smekal-Raman-Effekt", p. 223, 328. Dadieu, Kohlrausch, and Pongratz, *Manatsh.*, **60** (1932), 253; **61** (1932), 426; **63** (1933), 427; **64** (1934), 361, 374; **65** (1934), 6. Murray and Andrews, *J. Chem. Physics*, **1** (1933), 400; **2** (1934), 119.

(2) S. Ziemecki, *Z. Physik*, **78** (1932), 126.

(3) H. Gockel, *Z. physik. Chem.*, B, **29** (1935), 79.

(4) G. B. Bonino and P. Cella, *Atti accad. Lincei*, **13** (1931), 784; **15** (1932), 572.

(5) S. K. Mukerji, *Nature*, **134** (1934), 811.

(6) *Memoria dei Prof. G. B. Bonino e Dott. M. Ansidei letta alla R. Accademia delle Scienze dell' Instituto di Bologna*, 1934.

All the substances were redistilled over metallic sodium before use. The distillation being carried out in vacuum except in the cases of benzene and cyclohexane. The physical constants measured by Dr. Kageyama and the boiling point observed in our laboratory are tabulated in Table 1. The Raman spectra were photographed with a spectrograph of three prisms(7). About 12 c.c. of each substance was used. The Raman spectra of decahydro-pyrene and perhydro-pyrene could hardly be obtained without the use of the filter solution. The data for them seem to be incomplete on account of their strong back ground of the plate, which can not be removed even under the filtered mercury light. The experimental results are shown in Tables 3–14. The numbers of the Raman lines (n), the number of the plate, and the conditions under which the spectra were taken, are indicated in Table 2.

Table 1. Physical Constants of the Substances.

Substance	B.p. °C./mm. (Hg)*		n_D^{25}	d_4^{25}
Benzene	80.5/760	80.5/760	1.4992	0.8728
Cyclohexane	80.7/760	80.7/760	1.4250	0.7734
Phenyl-cyclohexane	92/5	80–82/3.5	1.5225	0.9339
Di-cyclohexyl	94/10	92.5–94.5/9.7	1.4820	0.8853
Tetrahydro-naphthalene	71–72/6	75–76/6.8	1.5410	0.9666
Decahydro-naphthalene	63/9	68/14.2	1.4770	0.8847
Tetrahydro-acenaphthene	98/5	97.5–99.5/3.6	1.5582	1.0115
Decahydro-acenaphthene	80/5	99–100/9.7	1.5016	0.9456
Decahydro-pyrene	160/5	162–163/5.4	1.5782	1.0553
Perhydro-pyrene	164/10	138–140/5.5	1.5225	0.9875
Indene	62/10		1.5755	0.9813

* Boiling points shown in the first column were observed in our laboratory.

Table 2.

Substance	No. of table	n	No. of plate	Width of slit (10^{-2} mm.)	Temp. (°C.)	Time of exposure (hours)
Benzene	3	45	135	90	24	7
			160	70	15	7
			273	64	25	12
			274	70	25	10

(7) This Bulletin, **9** (1934), 328.

Table 2. (*Concluded*)

Substance	No. of table	n	No. of plate	Width of slit (10^{-2} mm.)	Temp. (°C.)	Time of exposure (hours)
Cyclohexane	4	66	130	90	24	6
			131	100	24	4
			150	80	13	5
			151	90	14	6
			277	64	23	15
			278	70	23	40
Phenyl-cyclohexane	5	79	118	80	25	4
			155	90	15	7
			157	76	15	5
			279	70	20	10
			280	64	24	7
			281	70	24	7
Dicyclohexyl	6	58	152	80	13	7
			153	80	14	5
Indene	7	65	275	70	25	8
			276	76	26	18
Naphthalene (in Alcohol)	8 (a)	14	141	90	22	14
			142	96	22	15
			177	64	19	15
Naphthalene (in Benzene)	8 (b)	14	181	70	18	15
Tetrahydro-naphthalene	9	87	159	70	15	6
			161	64	15	7
			217	62	30	15*
Decahydro-naphthalene	10	69	154	90	14	7
			156	80	15	6
Tetrahydro-acenaphthene	11	79	163	60	15	7
			164	60	15	10
Decahydro-acenaphthene	12	68	158	76	15	8
			162	60	14	10
Decahydro-pyrene	13	32	166	60	15	10
			167	70	15	8
Perhydro-pyrene	14	42	235	76	15	12
			236	70	28	16*

* A solution of sodium nitrite was used as the filter.

Table 3. Benzene.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24440	3	q-2948	24	22253	1/2	e- 685(k-2452)
2	24406	2	p-2947	25	22158	1/2	e- 780(k-2547)
3	24338	5	q-3050(o-2955)	26	22139	1/2	f- 856
4	24304	1	k- 401(p-3049)	27	22087	5	e- 851
5	24289	4	p-3064	28	22054	1/2	g- 985
6	24225	4	q-3163(o-3068)	29	22047	1/2	g- 992
7	24203	3	q-3185	30	22003	1	f- 992
8	24165	1	p-3188	31	21958	2	e- 980
9	24101	5	k- 604	32	21945	10	e- 993
10	23931	2	(e+ 992)	33	21758	8	e-1180(k-2947)
11	23910	1	i- 606(k-795)	34	21654	6	k-3051
12	23857	4(b)	k- 848	35	21641	8(d)	k-3064
13	23724	2	k- 981	36	21567	1/2	i-2949
14	23712	10	k- 993	37	21539	2(b)	k-3166(e-1399)
15	23676	1/2	i- 840(k-1029)	38	21519	3	k-3186
16	23531	5	k-1174(i-985)	39	21463	3	i-3053
17	23524	8	i- 992	40	21452	5	i-3063
18	23339	2(d)	i-1177	41	21352	6	e-1586(i-3164)
19	23302	2	k-1403	42	21332	5	e-1606(i-3184)
20	23121	6	k-1584	43	19988	3	e-2950
21	23101	5	k-1604	44	19887	3	e-3051
22	22534	1/2(d)	e -404	45	19874	5	e-3064
23	22333	8	e -605				

$\Delta\nu$: 404 (1/2d); 605 (8); (685) (1/2); (780) (1/2); 849 (5); (981) (2); 993 (10); (1029) (1/2); 1176 (5); 1401 (2); 1585 (6); 1605 (5); (2452) (1/2); (2547) (1/2); 2948 (6); 3051 (6); 3064 (8d); 3166 (2b); 3186 (3).

Table 4. Cyclohexane.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24535	5	q-2853	5	24438	3(b)	o-2855
2	24500	3	p-2853(q-2888)	6	24430	3	p-2923
3	24464	4	q-2924(p-2889)	7	24414	3	p-2939
4	24450	4	q-2938	8	24367	3	o-2926

Table 4. (*Concluded*)

No.	ν	*I*	$\nu_0-\Delta\nu$	No.	ν	*I*	$\nu_0-\Delta\nu$
9	24351	3	o-2942	38	22016	1(d)	g-1023
10	24325	0	k- 380	39	22008	3	k-2697
11	24278	1	k- 427	40	21969	1/2	f-1026
12	23904	8	k- 801	41	21943	0	k-2762
13	23739	1	e- 801	42	21912	8	e-1026
14	23714	3	i- 802	43	22855	10	k-2850
15	23677	6(d)	k-1028	44	22838	2	f-1158
16	23550	3	k-1155	45	22820	5(b)	k-2885
17	23489	1(d)	i-1027	46	22785	8	e-1153(k-2920)
18	23442	8	k-1263	47	22768	8	k-2937
19	23362	2(d)	{ k-1343(i-1154) (e+424)	48	22673	8	e-1265(i-2843)
20	23298?	0(d)	k-1407	49	22629	1(d)	i-2887
21	23279	1/2	k-1426	50	22596	6	e-1342(i-2920)
22	23261	8(d)	k-1444(i-1255)	51	21579	5	i-2937
23	22240	1/2	k-1465	52	21553	1/2	f-1442
24	23222	0	k-1483	53	21534?	0	e-1404
25	23073	2	i-1443	54	21514	1/2	e-1424
26	22736	1/2	e- 202	55	21495	10	e-1443
27	22555	3(d)	e- 383	56	21474	1/2	e-1464
28	22514	4	e- 424(k-2349)	57	21452	1/2	e-1486
29	22356	1/2(b,d)	k-2349	58	20592	1/2(d)	e-2346
30	22239	2(b,d)	k-2466(e-699)	59	20477	1/2	e-2461(Hg)
31	22195	1	f- 800	60	20312	1	e-2626
32	22171	1/2	e- 767(k-2534)?	61	20277	2	e-2661
33	22154	1	e- 784(k-2552)?	62	20241	1	e-2697
34	22136	10	e- 802	63	20088	8	e-2850
35	22105	1/2(d)	e- 833(k-2600)	64	20054	3	e-2884(f-2941)
36	22076	2	k-2629	65	20017	6	e-2921
37	22041	5(d)	k-2664	66	20001	6	e-2937

$\Delta\nu$: 202 (1/2) ; 382 (3d) ; 425 (4) ; (699) (2b,d) ; (767) (1/2) : (784) (1) ; 802 (10) : (833) (1/2d) ; 1026 (8) ; 1154 (4) ; 1264 (8) ; 1342 (3) ; 1405 (0) ; 1425 (1/2) ; 1444 (10d) ; 1465 (1/2) ; 1485 (1/2) ; 2347 (1/2d) ; 2463 (1/2) ; (2534) (1/2) ; (2552) (1) ; 2600 (1/2d) ; 2628 (2) ; 2663 (5d) ; 2697 (3) ; (2762) (0) ; 2850 (10) ; 2885 (3) ; 2920 (8) ; 2937 (8).

Table 5. Phenyl-cyclohexane.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24604	2(d)	k- 101	38	22700	1/2(d)	e- 238
2	24459	2(bb,d)	q-2929	39	22661	6	e- 277
3	24429	3	k- 276	40	22578?	0(b,d)	e- 360
4	24345?	1/2(d)	k- 360	41	22556?	0(b,d)	e- 382
5	24327	1/2	k- 378	42	22529	1/2	e- 409
6	24292	1	k- 413(p-3061)	43	22502	2	e- 436
7	24268?	0	k- 437	44	22478	2	e- 460
8	24239	1/2(d)	k- 466(i-277)	45	22317	6	e- 621
9	24083	2	k- 622	46	22245?	0	f- 752
10	23965	1/2	k- 740	47	22197	1(d)	e- 741
11	23933	2	k- 772	48	22165	5	e- 773
12	23878	2	k- 827	49	22130?	0	f- 865
13	23868	1	k- 837	50	22111	3	e- 827
14	23842	1	k- 863	51	22097	1(d)	e- 841
15	23811	1/2	k- 894	52	22077	3	e- 861
16	23710	4	k- 995	53	22044	2(d)	e- 894
17	23702	4	k-1003	54	22013	1/2	e- 925(k-2692)
18	23674	4	k-1031	55	(21943	10	e- 995
19	23658	2(d)	k-1047	56	21937)	10	e-1001
20	23626	1(b,d)	k-1079	57	21909	6	e-1029
21	23587?	0	k-1118	58	21889	4	e-1049
22	23573?	0	k-1132	59	21854	8(b,d)	k-2851(e-1084)
23	23549	2	k-1156	60	(21814	3(b,d)	e-1124
24	23528	2	k-1177	61	21807)		e-1131
25	23506	3(d)	k-1199	62	21785	6(d)	e-1153
26	23476	1(d)	k-1229	63	21773	5(d)	k-2932
27	23443	2	k-1262	64	21764	4	e-1174
28	23426	4	k-1279	65	21740	5	e-1198
29	23408	1/2	k-1297	66	21710	4	e-1228
30	23377?	1/2(d)	k-1328	67	21676	4(b)	e-1262
31	23354?	0(d)	k-1351	68	21656	6	e-1282
32	23264	5(d)	k-1441	69	21641	4	k-3064(e-1297)
33	23216	2	e+ 278	70	21610	1(d)	e-1328
34	23102	5(b,d)	k-1603	71	21591	1(d)	e-1347
35	22827?	2(bb,d)	e- 111	72	21498	5	e-1440
36	22797	1/2	e- 141	73	(21364	1(b)	e-1574
37	22781	1/2(d)	e- 157	74	21357)		e-1581

Table 5. (*Concluded*)

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
75	21341	6	e-1597	78	20006	4(bd)	e-2932
76	21330	5	e-1608	79	19878	$^1/_2$	e-3060
77	20086	4	e-2852				

$\overline{\Delta\nu}$: 106 (2b,d)? ; (141) ($^1/_2$d)? ; (157) ($^1/_2$d)? ; 238 ($^1/_2$d) ; 277 (6) ; 360 ($^1/_2$d)? ; 380 ($^1/_2$) ; 411 ($^1/_2$) ; 437 (2) ; 460 (2) ; 621 (6) ; 741 (1d) ; 773 (5) ; 827 (3) ; 839 (1d) ; 862 (3) ; 894 (2d) ; (925) ($^1/_2$)? ; 995 (10) ; 1002 (10) ; 1030 (6) ; 1048 (4) ; 1082 (3b,d) ; $\left(\begin{matrix}1121\\1132\end{matrix}\right.$ (3b,d) ; 1155 (6d) ; 1175 (4) ; 1198 (5) ; 1229 (4) ; 1262 (4) ; 1281 (6) ; 1297 (1) ; 1328 (1d) ; 1349 (1d) ; 1440 (5) ; $\left(\begin{matrix}1574\\1581\end{matrix}\right.$ (1b) ; 1597 (6) ; 1608 (5) ; (2692) ($^1/_2$)? ; 2852 (4) ; 2932 (4) ; 3062 (3).

Table 6. Di-cyclohexyl.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24458	4(bb,d)	k- 247(q-2930)	22	23260	6(d)	k-1445
2	24435	4(d)	p-2918(o-2858)	23	23212	1(d)	k-1493
3	24345	2(b,d)	k- 260	24	23166	$^1/_2$(d)	i-1350
4	24268	1	k- 437	25	22836	1(d)	e- 102
5	24244	2	k- 461	26	22799	1(d)	e- 139
6	24219	2	k- 486	27	22767	$^1/_2$(d)	e- 171
7	23938	4	k- 767	28	22692	1	e- 246
8	23920	3	k- 785	29	22620	3(b)	e- 318
9	23903	1	k- 802	30	22574	1(d)	e- 364
10	23859	4	k- 846	31	22554	$^1/_2$(d)	e- 384
11	23746	1	k- 959(i-770)	32	22504	1	e- 434(f-486)
12	23728?	$^1/_2$	i- 788	33	22479	2	e- 459
13	23702	1(d)	k-1003	34	22454	2	e- 484
14	23668	5(b,d)	k-1037	35	22426	1	e- 512
15	23622	2	k-1083	36	22173	4	e- 765
16	23590	2	k-1115	37	22151	3	e- 787
17	23543	2	k-1162	38	22137	1	e- 801
18	23508	1(d)	k-1197	39	22092	5	e- 846
19	23463	0	k-1242	40	22044	1(b,d)	k-2661
20	23441	4(b)	k-1264	41	21980	1	e- 958
21	23356	3	k-1349(i-1160)	42	21936	2	e-1002

Table 6. (*Concluded*)

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
43	21899	5(b.d)	e–1039	51	21586	4	e–1352
44	21854	10	e–1084(k–2851)	52	21495	8(d)	e–1443
45	21817	3(d)	e–1121(k–2888)	53	21448	0	e–1490
46	21781	8(d)	e–1157(k–2924)	54	20273	1	e–2665
47	21768	8(d)	k–2937	55	20082	5	e–2856
48	21738	2(b)	e–1200	56	20–45	2	e–2893
49	21698	2	e–1240	57	(20020	5(b)	e–2918
50	21669	6(d)	e–1269	58	(19998		e–2940

$\Delta\nu$: 102 (1d)? ; 139 (1d ? ; 171 ($^1/_2$d)? ; 246 (1) ; 318 (3b) ; 364 (1d) ; 384 ($^1/_2$)? ; 435 (1) ; 460 (2) ; 485 (2) ; (512) (1) ; 766 (4) ; 787 (3) ; 801 (1) ; 846 (5) ; 958 (1) ; 1002 (2) ; 1038 (5b,d) ; 1083 (5) ; 1118 (3d) ; 1160 (3d) ; 1199 (2b) ; 1240 (2) ; 1267 (6d) ; 1351 (4) ; 1444 (8d) ; 1493 (1d) ; 2663 (1) ; 2853 (5) ; 2890 (2) ; (2921, 2939)(8b.d).

Table 7. Indene.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24463	$^1/_2$	p–2890	19	23392	2	k–1313
2	24315	$^1/_2$(d)	(k– 390(i–201) (q–3073)	20	23345	8	k–1360
3	24280	1(b,d)	p–3073	21	23312	6	k–1393(i–1204)
4	24171	3	k– 534	22	23302	$^1/_2$?	i–1214
5	24114	3(d)	k– 591	23	23248	8	k–1457
6	23975	6	k– 730	24	23155	10(b)	k–1550(i–1361)
7	23941	1	k– 764	25	23118	4	k–1587(i–1398)
8	23876	3(d)	k– 829	26	23096	10	k–1609
9	23844	3	k– 861	27	22734	3(d)	e– 204
10	23783	$^1/_2$(d)	k– 922(i–733)	28	22559	2	e– 379
11	23760	2(b)	k– 945	29	22547	2	e– 391
12	23686	8	k–1019(i–830)	30	22404	8	e– 534(f–591)
13	23638	5	k–1067	31	22347	6(d)	e– 591
14	23592	6(b,d)	k–1113	32	22208	10	e– 730
15	23554	2(d)	k–1151	33	22177	3(d)	e– 761
16	23499	10	k–1206(i–1017)	34	22108	5(d)	e– 830
17	23478	6(d)	d–1227	35	22097	2	e– 841
18	23421	2	k–1284	36	22078	5	e– 860

Table 7. (*Concluded*)

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
37	22026	1(d)	e- 912	52	21631	5(b)	e-1307(k-3074)
38	22013	1(d)	e- 925	53	21603	1(d)	f-1392
39	21994	5(bb)	e- 944	54	21592	2(d)	k-3113
40	21969	1(bd)	f-1026	55	21579	10	e-1359
41	21921	10	e-1017	56	21544	8(d)	e-1394(i-1451)
42	21870	6	e-1068	57	21481	10	e-1457
43	21832	6(bd)	e-1106	58	21448	2	e-1490(i-1547)
44	21820	5(bd)	k-2885	59	21408	1	i-1587
45	21797	1/2(d)	f-1198	60	21388	10	e-1550(f-1607)
46	21785	3(d)	e-1153	61	21351	5	e-1587
47	21773	1(d)	f-1222	62	21329	10	e-1609
48	21735	10	e-1203	63	20048	4(b)	e-2890
49	21714	6(d)	e-1224(f-1281)	64	19872	3(b,d)	e-3066
50	21669	7(db)	k-3036	65	19825	2(d)	e-3113
51	21651	5	e-1287				

$\Delta\nu$: 204 (3d); (379) (2); 391 (2); 532 (8); 591 (6d); 730 (10); 762 (3d); 830 (5d); (841) (2); 860 (5); (912) (1d); 923 (1d); 944 (5bb); 1018 (10); 1067 (6); 1110 (6b,d); 1152 (3d); 1204 (10); 1225 (6d); 1285 (5); 1310 (5b); 1359 (10); 1394 (8d); 1457 (10); (1490) (2); 1550 (10); 1587 (5); 1609 (10); 2890 (4); (3036) (2b,d); 3066 (3b,d); 3113 (2d).

Table 8(a). Naphthalene (in Alcohol).

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24458	5(b,d)	q-2930	23	22177	5	e- 761
2	(24428	5(b,d)	p-2925	24	22055	6(d)	e- 883
3	(24416	5(b,d)	q-2972	25	21989	1/2	k-2716
4	24380	2(d)	p-2973	26	21943	1/2	f-1052
5	24364	2(d)	o-2929	27	21912	3	e-1026
6	24227	1/2	o-3066	28	21889	3(d)	e-1049(k-2818)
7	24193	3	k- 512	29	21840	5(b,d)	e-1098
8	23942	4	k- 763	30	21823	5(b,d)	k-2882(e-1115)
9	23821	5(d)	k- 884	31	21776	8(b,d)	k-2929(e-1162)
10	23676	3	k-1029	32	21733	6(d)	k-2972
11	23654	3(d)	k-1051	33	21662	4(d)	e-1276
12	23607	2)d)	k-1098	34	21632	5(d)	k-3073
13	23542	1	k-1163	35	21585	2	i-2931
14	23432	3(d)	k-1273	36	21557	10	e-1381
15	23324	8	k-1381	37	21488	6(b,d)	e-1450
16	23252	5(d)	k-1453	38	21475	6(b,d)	e-1463
17	23242	5(d)	k-1463(i-1274)	39	21460	1	e-1478
18	23137	3	i-1379	40	21356	3	e-1582
19	23126	3	k-1579	41	20056	5(b,d)	e-2882
20	22514	2(d)	e- 424	42	20011	6(b,d)	e-2927
21	22492	1/2(d)	e- 446	43	19964	6(b,d)	e-2974
22	22424	5	e- 514	44	19870	1	e-3068

$\Delta\nu$: (Alcohol) 424 (2d); 446 (1/2d); 883 (6d); 1050 (3d); 1098 (5b,d); (1115) (1); 1162 (2); 1275 (4d); 1451 (6b,d); (1478) (1); (2716) (1/2); 2818 (3d); 2882 (5d); 2928 (8b,d); 2973 (6d).

$\Delta\nu$: (Naphthalene) 513 (5); 762 (5); 1027 (3); 1381 (10); 1463 (5d); 1581 (3); 3070 (5d).

Table 8 (b). Naphthalene (in Benzene).

No.	ν	*I*	$\nu_0-\Delta\nu$	No.	ν	*I*	$\nu_0-\Delta\nu$
1	24440	2(d)	q-2948	23	22161	1	e- 777
2	24321	4	q-3067	24	22087	3	e- 851
3	24286	4	p-3067	25	22003	1(d)	f- 992
4	24225	4	o-3068	26	21958	1	e- 980
5	24191	5	k- 514	27	21945	10	e- 993
6	24101	5	k- 604	28	21910	4	e-1028
7	23941	6	k- 764	29	21788	1	e-1150
8	23926	2	k- 779	30	21763	5(d)	e-1175
9	23857	1(d)	k- 848	31	21654	6	k-3051
10	23724	2	k- 981	32	21641	8(d)	e-1297(k-3064)
11	23712	8	k- 993	33	21555	8	e-1383
12	23677	3	k-1028	34	21539	1	k-3166
13	23556	1/2	k-1149	35	21519	2	k-3186
14	23527	5	k-1178	36	21474	4(b, d)	e-1464
15	23323	8	k-1382	37	21449	3	e-1489
16	23241	5	k-1464	38	21419	1/2	f-1576
17	23129	5(b, d)	k-1576	39	21360	4(b, d)	e-1578
18	23121		k-1584	40	21354	4(b, d)	e-1584
19	23101	2	k-1604	41	21332	3	e-1606
20	22424	6	k- 514	42	19990	3	e-2948
21	22328	6	e- 610	43	19887	3	e-3051
22	22174	6	e- 764	44	19874	6	e-3064

$\overline{\Delta\nu}$: (Benzene) 607 (6); 778 (1); 849 (3); 980 (1); 993 (10); 1176 (5d); 1584 (4b); 1605 (3); 2948 (3); 3051 (6); 3064 (8d); 3166 (1); 3816 (2).
$\overline{\Delta\nu}$: (Naphthalene) 514 (6); 764 (6); 778 (1)?; 1028 (4); 1382 (8); 1464 (4); 1577 (4); (3064) (8).

Table 9. Tetrahydro-naphthalene.

No.	ν	*I*	$\nu_0-\Delta\nu$	No.	ν	*I*	$\nu_0-\Delta\nu$
1	24590	3(d)	k- 115	10	24193	2(b)	k- 512
2	24540	4(d)	k- 165	11	24118	3	k- 587
3	24466	1	p-2887	12	24000	2	k- 705(i-516)
4	24441	4(d)	k- 264(q-2947)	13	23977	5	k- 728
5	24404	3	p-2949	14	23960	1/2	k- 745
6	24346	2(b, d)	i- 170(q-3042)	15	23938	1	k- 767
7	24305	2(d)	p-3048	16	23897	2	k- 808
8	24268	3	k- 437	17	23881	3	k- 824
9	24247	2	k-456(i-269)	18	23832	1	k- 873

Table 9. (*Concluded*)

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
19	23782	2	i- 734	54	22031	2(b, d)	e- 907(k-2674)
20	23714	2	i- 802	55	21987	2(d)	e- 941(k-2713)
21	23691	1/2	i- 825	56	21948	3	f-1047
22	23664	8	k-1041	57	21927	1	f-1068
23	23634	3(b, d)	k-1071	58	21898	10	e-1040
24	23589	1/2(d)	k-1116	59	21867	8	e-1071
25	23541	4(d)	k-1164	60	21839	6	k-2866(f-1156)
26	23498	6	k-1207	61	21819	6	k-2886(e-1119)
27	23473	2(d)	k-1232(i-1043)	62	21792	6(b)	k-2913(f-1203)
28	23415	3	k-1290	63	21773	6(b)	e-1165
29	23402	3	k-1303	64	21757	6(b)	k-2948(f-1238)
30	23358	5	k-1347	65	21734	8	e-1204
31	23344	3	k-1361	66	21700	3	e-1238
32	23320	6	k-1385	67	21678	3	k-3027
33	23269	6	k-1436	68	21660	5	k-3045(f-1335)
34	23251	3	k-1454	69	21640	4	e-1298(f-1355)
35	23240	3(d)	k-1465	70	21626	1/2(d)	i-2890
36	23194	2(d)	e+ 256	71	21595	4	e-1343
37	23121	3(d)	k-1584	72	21579	4	e-1359
38	23103	6(d)	k-1602	73	21553	5	e-1385
39	22819	5(d)	e- 119	74	21505	6	e-1433
40	22774	6(b, d)	e- 164	75	21488	3	e-1450
41	22669	4(d)	e- 269	76	21476	3	e-1462
42	22620	1(d)	e- 318	77	21442	1/2(b, d)	e-1496
43	22503	6	e- 435	78	21355	4	e-1583
44	22480	4	e- 458(f-515)	79	21335	6	e-1603
45	22428	4(b)	e- 510	80	20073	4	e-2865
46	22354	6	e- 584	81	20053	4	e-2885
47	22234	3	e- 704(f-761)	82	20023	3(d)	e-2915(Hg)
48	22210	8	e- 728	83	19998	5	e-2940
49	22191	1	e- 747(f-804)	84	19958	1/2(d)	f-3037
50	22173	3	e- 765(f-822)	85	19937	1/2	f-3058
51	22130	3	e- 808	86	19907	3(d)	e-3031
52	22117	4(d)	e- 821	87	19895	4	e-3043
53	22066	3	e- 872				

$\overline{\Delta\nu}$: 117 (5d); 164 (6b, d); 267 (4d); (318) (1/2d); 436 (6); 457 (4); 511 (4b); 585 (6); 704 (3); 728 (8); 746 (1); 766 (3); 808 (3); 822 (4d); 872 (3); (907) (2b, d); (941) (2d); 1040 (10); 1071 (4); 1117 (1/2d); 1164 (6b); 1205 (8); 1235 (3); 1284 (3); 1301 (3); 1345 (4); 1360 (4); 1385 (5); 1435 (6); 1452 (3); 1463 (3); (1496) (1/2b, d); 1583 (4); 1602 (6); (2674) (2b, d); (2713) (2d); 2866 (6); 2885 (6); 2914 (3d) ?; 2994 (6b); 3029 (3d); 3044 (5).

Table 10. Decahydro-naphthalene.

No.	ν	*I*	$\nu_0-\Delta\nu$	No.	ν	*I*	$\nu_0-\Delta\nu$
1	24533	3(bb, d)	k- 172(q-2855)	36	22445	4	e- 493
2	24490	3(d)	q-2898(p-2863)	37	22337	4	e- 601
3	(24466	3(bb, d)	q-2922	38	22233	1/2	f- 762
4	(24416	3(bb, d)	p-2937(k-289)	39	22199	1/2	f- 796
5	24374	2(d)	k- 331	40	22187	6	e- 751
6	24352	2(d)	k- 353(i-164)	41	22178	3(d)	e- 760
7	24296	3	k- 409	42	22136	3	e- 802
8	24217	3	k- 488	43	22082	5	e- 856
9	24104	3	k- 601(i-412)	44	22062	3	e- 876
10	23954	3	k- 751	45	22041	3(d)	k-2664
11	23947	1	k- 758	46	22008	1(d)	e- 930(f-987)
12	23902	1/2	k- 803	47	(21960	3(b, d)	e- 978
13	23848	3	k- 857	48	(21949		e- 989(f-1046)
14	23828	1/2	k- 877	49	21919	3	e-1019
15	23771	1/2	k- 934	50	21891	4	e-1047
16	23715	2(b, d)	k- 990(i-801)	51	21877	3(b, d)	e-1061
17	23685	1	k-1020	52	21847	8(b, d)	k-2858(f-1148)
18	23658	4	k-1047(i-858)	53	21809	4	k-2896
19	23645	3	k-1060(i-871)	54	(21788	8	(k-2917(e-1150)
20	23555	1/2	k-1150	55	(21770	8(b, d)	(k-2935(e-1168)
21	23533	2(d)	k-1172(e+595)	56	(21762	8(b, d)	e-1176
22	23455	3	k-1250(i-1061)	57	21711	1/2	f-1284
23	23446	3	k-1259	58	21702	1/2	e-1236 ?
24	23432	3	k-1273(e+494)	59	21690	4	e-1248
25	23350	1	k-1355(e+412)	60	21678	4	e-1260
26	23335	3	k-1370	61	21661	4	e-1277(i-2855)
27	23251	4(d)	k-1454(i-1265)	62	21587	4(d)	e-1351(i-2925)
28	(22786	1(b, d)	e- 152	63	21570	4(d)	e-1368
29	(22766	1(b, d)	e- 172	64	21487	6(b, d)	e-1451
30	22641?	0	e- 297	65	20280	0	e-2658
31	22610	2(d)	e- 328	66	20082	6	e-2856
32	22579	2	e- 359	67	20041	3	e-2897
33	22557	2	e- 381	68	(20022	6(b)	e-2916
34	22530	5	e- 408	69	(20002		e-2936
35	22496?	1/2(d)	e- 442				

$\overline{\Delta\nu}$: 152–172 (1bb, d); 297 (0); 329 (2d); 356 (2); (381) (2); 408 (5); (442) (1/2d); 491 (4); 601 (4); 751 (6); 759 (3d); 802 (3); 856 (5); 876 (3); 932 (1d); 990 (3b, d); 1020 (3); 1047 (4); 1060 (3b, d); 1150 (1); 1170 (2); (1236) (1/2); 1249 (4); 1260 (4); 1275 (4); 1353 (4d); 1369 (4d); 1452 (6b, d); 2661 (3d); 2857 (8b, d); 2896 (4); (2916, 2936) (8b, d).

Table 11. Tetrahydro-acenaphthene.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	24575	1(d)	k- 130	38	22690	4(d)	e- 248
2	24548	2(d)	k- 157(q-2840)	39	22557	4	e- 381
3	24485	1/2(d)	k- 220	40	22536	2	e- 402(f-459)
4	24453	3(b, d)	k- 252(q-2935)	41	22497	1	f- 498
5	24302	1/2(d)	k- 403	42	22481	7	e- 457
6	24251	3	k- 454	43	22431	4(d)	e- 507(f-564)
7	24199	2(d)	k- 506	44	22370	8	e- 568
8	24136	5(b)	k- 569	45	22348	5	e- 590(f-647)
9	24113	2	k- 592(i-403)	46	22331	0	e- 607
10	24099	1/2	k- 606	47	22288	10	e- 650
11	24056	6	k- 649	48	22215	1/2(d)	e- 723(k-2490)
12	23944	1(d)	k- 761	49	22172	2	e- 766
13	23908	3	k- 797	50	22138	6	e- 800
14	23866	1/2	i- 650	51	22112	1	e- 826(k-2593)
15	23847	1/2	k- 858	52	22080	2	e- 858
16	23764	1	k- 941	53	22066	1	e- 872(k-2639)
17	23750	1	k- 955	54	22037	3(b, d)	k- 2668(f-958)
18	23676	6	k-1029	55	22001	3	e- 937
19	23644	5	k-1061	56	21987	3	e- 951
20	23610	1/2	k-1095	57	21963?	1/2	f-1032
21	23578	2	k-1127(i-938)	58	21908	8	e-1030
22	23550	2	k-1155	59	21877	6	e-1061(f-1118)
23	23525	0	k-1183	60	21865	7(b)	k-2840
24	23498	1/2	i-1018	61	21843	4	e-1095(k-2862)
25	23483	6	k-1222	62	(21822	3	e-1116
26	23453	2	k-1252(i-1063)	63	21808)	3	e-1130(f-1187)
27	23429	2(b, d)	k-1276	64	21779	3	e-1159
28	23384	2	i-1132	65	21764	4	k-2941
29	(23369	4(b, d)	k-1336	66	21752	3	e-1186
30	23358)	5(b, d)	i-1158	67	21716	8	e-1222(f-1279)
31	23276	6	k-1429	68	21689	3	e-1249
32	23254	4	k-1451	69	21659	5(d)	{e-1279(k-3046) (f-1336)}
33	23154	4(d)	e+ 216	70	21599	6(b, d)	e-1339
34	23097	6(d)	k-1608	71	21504	8	e-1434
35	22808	3	e- 130	72	21486	6	e-1452
36	22773	6(b, d)	e- 165	73	21328	7(d)	e-1610
37	22718	6	e- 220	74	20273	1	e-2665

Table 11. (*Concluded*)

No.	ν	*I*	$\nu_0-\Delta\nu$	No.	ν	*I*	$\nu_0-\Delta\nu$
75	20099	3(d)	e-2839	78	19899	1(d)	e-3039
76	20088	1	e-2850	79	19869?	$^1/_2$(d)	e-3069
77	20000	5(b, d)	e-2938				

$\overline{\Delta\nu}$: 130 (3); 161 (6b, d); 220 (6); 250 (4d); 381 (4); 402 (2); 456 (7); 507 (4d); 568 (8); 591 (5); 607 ($^1/_2$)?; 650 (10); (723) ($^1/_2$ d)?; 764 (2); 799 (3); (826) (1)?; 858 (2); (872) (1); 939 (1); 953 (3); 1030 (5); 1061 (6); 1095 (4); (1116) (3); 1128 (3); 1157 (3); 1185 (3); 1222 (6d); 1250 (3); 1278 (5d); 1338 (5d); 1432 (8); 1452 (6); 1609 (7d); (2490) ($^1/_2$d)?; (2593) (1)?; (2639) (1)?; 2666 (3b, d); 2840 (7b); 2856 (2); 2940 (5b, d); 3043 (5d); (3069) (1/2 d)?.

Table 12. Decahydro-acenaphthene.

No.	ν	*I*	$\nu_0-\Delta\nu$	No.	ν	*I*	$\nu_0-\Delta\nu$
1	24454	2(b, d)	q-2934	26	22610	1	e- 328
2	24422	1(b, d)	p-2931	27	22580	$^1/_2$	e- 358
3	24404	$^1/_2$(d)	p-2949	28	22566	2(d)	e- 372
4	24380	$^1/_2$(d)	k- 325	29	22506	2	e- 432
5	24351	1(d)	k- 354	30	22488	1(d)	f- 507
6	24274	$^1/_2$	k- 431	31	22443	3(d)	e- 495
7	24203	$^1/_2$(d)	k- 502	32	22423	$^1/_2$(d)	e- 515
8	24159	$^1/_2$	k- 546	33	22390	4	e- 548
9	24084	1	k- 621	34	22373?	$^1/_2$	f- 622
10	23984	3	k- 721	35	22343	1	e- 595
11	23954	1	k- 751	36	22318	3	e- 620
12	23851	1	k- 854	37	22215	6	e- 723
13	23755	2	k- 950	38	22182	4	e- 756
14	23681	1	k-1024	39	22150	$^1/_2$	f- 845
15	23637	1(d)	k-1068	40	22129	1	e- 809
16	23607	$^1/_2$	k-1098	41	22105	1	k-2600
17	23587	0	i-1028	42	22084	3(d)	e- 854
18	23548	0	k-1157	43	22042	3(d)	k-2663
19	23469	$^1/_2$	k-1236	44	22028	2(d)	e- 910(k-2677)
20	23416	1(d)	k-1289	45	22011	2	k-2694
21	23333	1(d)	k-1372	46	21988	4	e- 950
22	23255	4(d)	k-1450	47	21957	2(d)	k-2748
23	23226	1	k-1479	48	21913	4	e-1025
24	22832	1(d)	e- 106	49	21894	2(b, d)	k-2761(f-1101)
25	22761	2(d)	e- 177	50	21870	8(b, d)	e-1068

Table 12. (*Concluded*)

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
51	21842	6(b, d)	e-1096	60	21567	5(b, d)	e-1371
52	21812	4	k-2893	61	21493	8(d)	e-1445
53	21773	8(b, d)	e-1165(k-2932)	62	21456	4(d)	e-1482
54	21756	6(b, d)	k-2949	63	20276	$^1/_2$(d)	e-2662
55	21726	1	e-1212 ?	64	20238	1(d)	e-2700
56	21702	2	e-1236	65	20087	4(b)	e-2851
57	21691	1	i-2934	66	20045	2	e-2893
58	21649	5(b, d)	e-1289	67	20013	6(b, d)	e-2925
59	21617	4(d)	f-1378	68	19996	6(b, d)	e-2942

$\Delta\nu$: (106) (1d) ?; (177) (2d); 326 (1); 356 ($^1/_2$); (372) (2d); 432 (2); 498 (3d); (515) ($^1/_2$d); 547 (4); (595) (1); 620 (3); 722 (6); 754 (4); (809) (1); 854 (3d); (910) (2); 950 (4); 1025 (4); 1068 (8b, d); 1096 (6b, d); 1161 (0); (1212) (1) ?; 1236 (2); 1289 (5b, d); 1371 (5b, d); 1448 (8d); 1481 (4d); (2600) (1); 2663 (3d); (2677) (2) ?; 2697 (2); (2748) (2d); (2761) (2d) ?; 2851 (4b); 2893 (4); 2925 (6b, d); 2942 (6b, d).

Table 13. Decahydro-pyrene.

No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	23484	$^1/_2$	k-1221	17	21877	6(b, d)	e-1061(k-2828)
2	23421	0	k-1284	18	21841	6(d)	k-2864(e-1097)
3	23344?	$^1/_2$	k-1361	19	21773	8(b, d)	k-2932
4	23252	$^1/_2$	k-1453	20	21717	5	k-1221
5	23100	2	k-1605	21	21660	0	e-1278
6	22758	2(b, d)	e- 158	22	21623	2	k-3082(e-1315)
7	22620?	$^1/_2$(d)	e- 318	23	21599	1	e-1339
8	22549	2(b, d)	e- 389	24	21577	3(d)	e-1361
9	22526?	$^1/_2$(d)	e- 412	25	21503	6(b, d)	e-1434
10	22413	2	e- 525	26	21490	6(d)	e-1448
11	22381	1	e- 557	27	21359	$^1/_2$(d)	e-1579
12	22352	2(b)	e- 586	28	21335	3(d)	e-1603
13	22324	1	e- 614	29	20114	4	e-2824
14	22296?	0(d)	e- 642	30	20081	2	e-2857
15	22128?	0	e- 810	31	20004	5(b, d)	e-2934
16	22047	4	e- 891	32	19850	$^1/_2$	e-3088

$\Delta\nu$: (158) (2b, d); (318) ($^1/_2$d) ?; (389) (2b, d); (412) (0d) ?; (525) (2); (557) (1); 587 (2b); (614) (1); (642) (0d) ?; (810) (0) ?; (891) (4); (1061) (6b, d); (1097) (6d); 1221 (5); 1281 (0); (1315) (2); (1339) (1); 1361 (3d); {1435 (6b, d); 1450 (6d)}; (1579) ($^1/_2$d); 1604 (3d); 2826 (4); 2861 (2bb, d); 2934 (5bb, d); 3085 (3).

Table 14. Perhydro-pyrene.

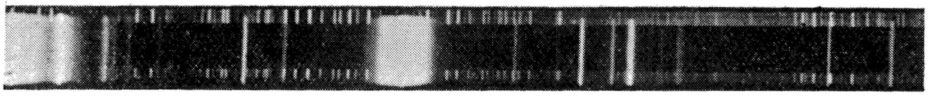
No.	ν	I	$\nu_0-\Delta\nu$	No.	ν	I	$\nu_0-\Delta\nu$
1	23402	1/2	e+ 464	22	22105	2	e- 833
2	23360	1(d)	k-1345	23	22076	2	e- 862
3	23349?	1/2	k-1356	24	21969	1/2	e- 969
4	23302?	1(b, d)	e+ 364	25	21929	1/2	e-1009
5	23263?	1/2	k-1442	26	21906	1/2	e-1032
6	23168	1	i-1447	27	21882	4	k-2823(e-1056)
7	22677	1(d)	e- 261(f-318)	28	21846	3	k-2859(e-1092)
8	22644	1	e- 294(f-351)	29	21790	4(b, d)	k-2915(e-1148)
9	22616	2	e- 322	30	21779	3(b, d)	k-2926(e-1159)
10	22587	3	e- 351	31	21721	1	e-1217
11	22566	2(d)	e- 372(f-429)	32	21709	4(d)	e-1229
12	(22518	4(b, d)	e- 420	33	21690	3(d)	e-1248
13	22512)	4(b, d)	e- 426	34	21647	1/2(b, d)	e-1291
14	22474	4(b)	e- 464	35	21611	0	e-1327
15	22448	1	e- 490	36	(21590	1	e-1348
16	22406	1	e- 532	37	21581)	4(b, d)	e-1357
17	22375	3	e- 563	38	21492	4(d)	e-1446
18	22304	1(b, d)	e- 634	39	20120	3	e-2818
19	22240	1(d)	e- 698	40	20093	3	e-2846
20	22195	4	e- 743	41	20028	5(b)	e-2910
21	22148	2	e- 790	42	20007	4(b)	e-2931

$\Delta\nu$: 261 (1d); 294 (1); 322 (2); 351 (3); 372 (2d); 420 (4b, d); 426 (4b, d); 464 (4b); 490 (1); 532 (1); 563 (3); 634 (1b, d); 698 (1d); 743 (4); 790 (2); 833 (2); 862 (2); (969) (1/2)?; 1009 (1/2); 1032 (1/2); (1056) (4); (1092) (3); (1148) (4b, d); (1159) (3b, d); 1217 (1/2); 1229 (4d); 1248 (3d); 1291 (1b, d); 1327 (0); 1348 (1); 1357 (4b, d); 1444 (4d); 2820 (3); 2853 (3); 2912 (4b); 2938 (4b).

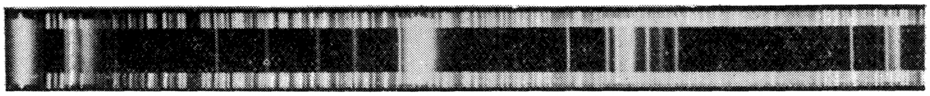
Discussion.

The Raman spectra of benzene and cyclohexane have been studied by several authors[(1)], especially by Wood and Collins[(8)] with the improved arrangement. The so-called "complete Raman spectrum of benzene" has been published by Grassman and Weiler[(9)]. In the present experiments the long exposure of 40 hours has been tried with cyclohexane in order to obtain a complete Raman spectrum of the substance. The result is compared with

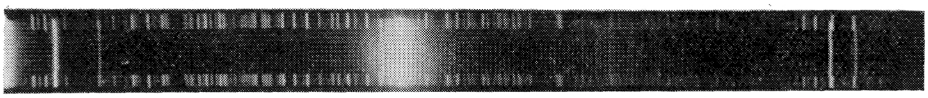
(8) R. Wood and G. Collins, *Phys. Rev.*, **42** (1932), 386.
(9) P. Grassman and J. Weiler, *Z. Physik*, **86** (1933), 321.



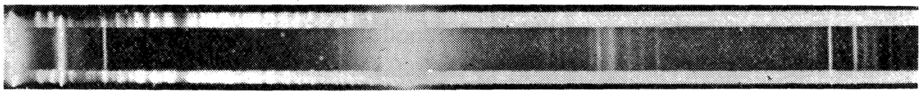
(1) Benzene



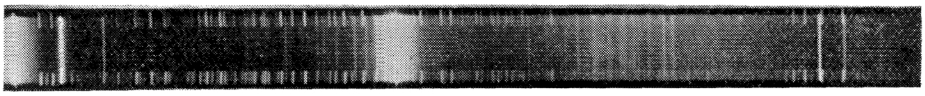
(2) Cyclohexane



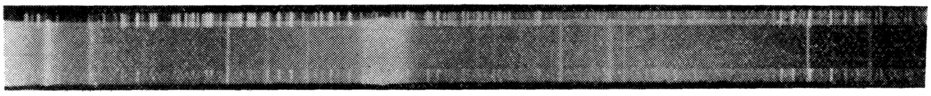
(3) Phenyl-cyclohexane



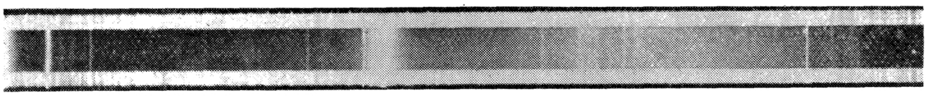
(4) Di-cyclohexyl



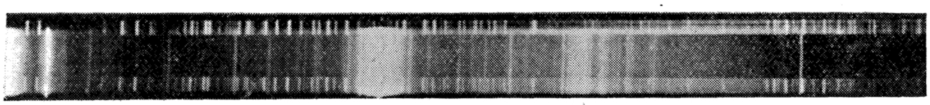
(5) Indene



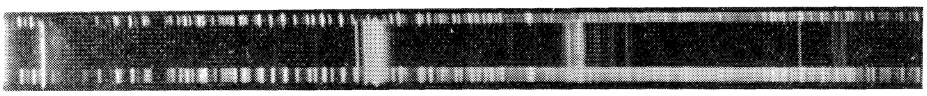
(6a) Naphthalene (in benzene)



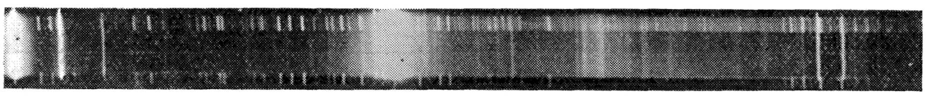
(6b) Naphthalene (in alcohol)



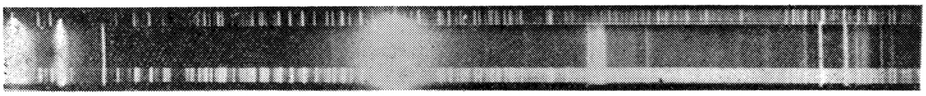
(7) Tetrahydro-naphthalene



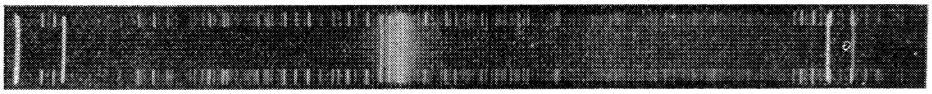
(8) Decahydro-naphthalene



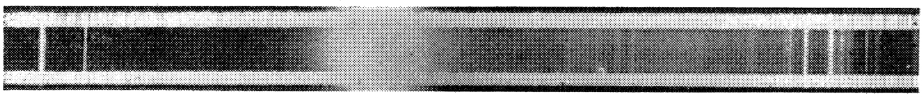
(9) Tetrahydro-acenaphthene



(10) Decahydro-acenaphthene



(11) Decahydro-pyrene



(12) Perhydro-pyrene

those obtained by Krishnamurti[10], and Wood and Collins[8] as shown in Table 15. Four new lines corresponding to $\Delta\nu$ 1405, 1425, 1465, and 1485 cm.$^{-1}$ are found to be accompanied with the deformation frequency of the CH_2-group. These lines are very weak and appear in the equal intervals of about 20 cm.$^{-1}$ As shown in Table 4 and Table 15, some other new lines of $\Delta\nu$ 22171, 22154

Table 15. Comparison of the Results with Cyclohexane.

Krishnamurti	Wood, Collins	Matsuno, Han	Krishnamurti	Wood, Collins	Matsuno, Han
—	—	202 (1/2)	—	—	1464 (1/2)
381 (1/2)	380 (2)	382 (3d)	—	—	1485 (1/2)
425 (1)	422 (3)	425 (4)	2351 (0)	—	2347 (1/2d)
695 (0)	—	(699) (2b,d)?	2462 (0)	—	2463 (1/2)
—	—	(767) (1/2)?	—	—	(2534) (1/2)?
—	—	(784) (1/2)?	—	—	(2552) (1)?
802 (10)	801 (10)	802 (10)	—	—	(2600) (5/2d)?
—	—	(833) (1/2d)?	2630 (0)	2626 (0)	2628 (3)
992 (0)?	—	—	2662 (1)	2661 (1)	2663 (5d)
1028	1026 (8)	1026 (8)	2696 (1/2)	2693 (0)	2697 (3)
1156 (1)	1154 (4)	1154 (4)	—	2750 (0)	(2762) (0)?
1266 (5)	1264 (8)	1264 (8)	2852 (8)	2849 (10)	2850 (10)
1344 (1/2)	1342 (2)	1342 (3)	2889 (1)	2880 (1)	2885 (2)
—	—	1404 (0)	2922 (8)	2920 (10)	2920 (8)
—	—	1424 (1/2)	2938 (8)	2934 (10)	2937 (8)
1444 (5)	1442 (10)	1444 (10d)			

(10) P. Krishnamurti, *Indian J. Physics*, **6** (1931), 543.

and 22105 cm.$^{-1}$ are observed also very weak. These lines may correspond to the shifts of $\Delta\nu$ 767, 784 and 833 cm.$^{-1}$ respectively, when they are assumed to have been excited by the 22938 cm.$^{-1}$ mercury line. These lines coincide, however, with the shifts of $\Delta\nu$ 2534, 2552 and 2600 cm.$^{-1}$ respectively, when they are assumed to have been excited by the 24705 cm.$^{-1}$ mercury line. The assignments of these new lines will be given by the experiments done by the longer exposure and by using the filter. The other intense Raman lines of $\Delta\nu$ 382, 425, 802, 1026, 1154, 1264, 1342, 1444, 2628, 2663, 2697, 2850, 2920, and 2937 cm.$^{-1}$ in cyclohexane have been observed by nearly all investigators.

If we ascribe most of the intense lines of these Raman shifts, i.e., $\omega_1 = 382(3)$, $\omega_2 = 425(4)$, $\omega_3 = 802(10)$, $\omega_4 = 1026(8)$, $\omega_5 = 1154(4)$, $\omega_6 = 1264(8)$, $\omega_7 = 1342(3)$, $\omega_8 = 2444(10)$, $\omega_9 = 2850(10)$, $\omega_{10} = 2920(8)$, $\omega_{11} = 2937(8)$, to the Raman-active fundamentals, most of the other weak lines may be probably associated with the harmonic or the combination frequencies of these fundamentals, as shown in Table 16.

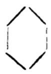
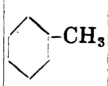
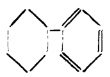
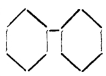
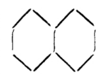
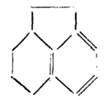
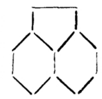
Table 16.

$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}$	$\omega_{obs.}$
$2\omega_1 = 764$	(767)	$2\omega_6 = 2528$	(2534)
$2\omega_2 = 850$	(833)	$2\omega_7 = 2684$	2697
$2\omega_5 = 2308$	2347	$2\omega_8 = 2888$	2885
$\omega_4 - \omega_3 = 224$	202	$\omega_9 - \omega_1 = 2468$	2466
$\omega_3 - \omega_1 = 420$	425 ($=\omega_2$)	$\omega_{10} - \omega_1 = 2538$	(2534)
$\omega_8 - \omega_4 = 418$		$\omega_{11} - \omega_1 = 2555$	(2552)
$\omega_5 - \omega_1 = 772$	(784)	$\omega_6 + \omega_7 = 2606$	(2600)
$\omega_6 - \omega_2 = 839$	(833)	$\omega_6 + \omega_8 = 2708$	2697
$\omega_9 - \omega_8 = 1406$	1405		
$\omega_1 + \omega_4 = 1408$			

In Table 17, Raman frequencies of cyclohexane, methyl- and phenyl-cyclohexane, di-cyclohexyl, decahydro- and tetrahydro-naphthalene, tetrahydro- and decahydro-acenaphthene are tabulated. The shifts associated with the benzene ring are excluded from this table. Data of methyl-cyclohexane, observed by Godchot[11], are cited for comparison.

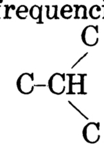
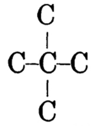
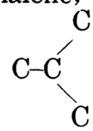
(11) Godchot, Canals, and Cauquil, *Compt. rend.*, **194** (1932), 176.

Table 17. Raman Frequencies associated with the Cyclohexane Ring.

								
ω_1	382	392	360 380	364 384	356 (381)	—	381	356 (372)
ω_2	425	444 775	411 437 460 741 773	435 460 766 787	408 751 759	436 457 704 728 746 766	402 456 764	432 722 754
ω	802	845 896 971	827 839 862 894 (925)	801 846 958	802 856 876 (932) 890	808 822 872 (907) (941)	799 (826) 858 (872) 939 953	(809) 854 (910) 950
ω_4	1026	1038	1048	1038	1047	1040	1030	1025
ω_5	1154	1167	1155 1175	1160	1150 1170	1164	1157	1161
ω_6	1264	1266	1262	1267	1249 1260 1275	1235 1284	1250 1278	1236 1289
ω_7	1342	1352	1349	1351	1353 1369	1345 1360 1385	1338	1371
ω_8	1444	1446	1440	1444	1452	1435 1452 1463	1432 1451	1448

All the fundamental frequencies in cyclohexane appear also in its mono-substitution products, viz., methyl-, phenyl-cyclohexane, and di cyclohexyl, as shown in Table 17. It is of interest, however, to note that some of these fundamentals, such as those of ca. $\Delta\nu$ 440, 845 and 1037 cm.$^{-1}$, which appear in the mono-substitution products, have higher values than in cyclohexane itself. This seems to indicate that the introduction of the aromatic or the aliphatic radicals has the effect of raising the force constants, or of sharpening the valency angle.. Further, when we take tetrahydro- and decahydro-naphthalene as the ortho-di-substitution products of cyclohexane, we find that most of the frequencies appear equal among these two substances, except the shift denoting ω_1, which disappears in the case of tetraphydronaphthalene. The frequencies corresponding to the fundamentals of the cyclohexane ring appear also in tetrahydro- and decahydro-acenaphthene which may lead to the consideration that they are 1,2,3-tri-substitution products of cyclohexane.

The displacement or the spalting of the fundamental frequencies, ω_2 and ω_3, and the decrease of the intensity of ω_3 in phenyl-cyclohexane and dicyclohexyl may be attributable to the disturbance of the symmetry of the cyclohexane ring by the adjacent benzene or cyclohexane ring, while the displacement or the spalting of ω_3, ω_6 and ω_7 in tetrahydro- and decahydro-naphthalene may be possibly attributable to the existence of the isomers, besides to the cause explained above.

In the previous paper[12], we ascribed the frequencies of $\Delta\nu$ 733–780, and 915–965 cm.$^{-1}$ to the valency frequencies of the  or  linkage. The fact that the frequencies in these regions are also observed in phenyl-cyclohexane, dicyclohexyl, tetrahydro- and decahydro-naphthalene, tetrahydro- and decahydro-acenaphthene which have the linkage of  seems to offer another verification for it (Table 17).

We may consider phenyl-cyclohexane as mono-derivative, indene, naphthalene and tetrahydro-naphthalene as di-derivatives (ortho), tetrahydro-acenaphthene as tri-derivative (1 : 2 : 3), and decahydro-pyrene as tetra-derivative (1 : 2 : 3 : 4), of benzene. In the case of phenyl-cyclohexane, the frequencies of $\Delta\nu$ 621, 1002, 1030, 1175–1198, 1597–1608 and 3062 cm.$^{-1}$ are taken as the characteristic lines of the mono-derivatives of benzene, corresponding to $\alpha = 616$, $\beta = (849)$, $\gamma = 1000$, $\xi = 1026$, $\delta = 1166$, and $\varepsilon = 1595$, as denoted by Dadieu, Pongratz and Kohlrausch[13]. These frequencies correspond also to those at $\Delta\nu$ 611, 833, 994, 1022, 1191, 1589–1609 and 3047 cm.$^{-1}$ in diphenyl which have been observed by Dadieu and Kohlrausch and by Wood[14]. The lower values of the Raman frequencies in diphenyl than in phenyl-cyclohexane may be attributable to the mutual effect of the benzene ring.

Dadieu, Pongratz, and Kohlrausch have reported that in the di-derivatives of benzene (ortho), only the frequencies of $\Delta\nu$ 3060 and 1595 cm.$^{-1}$ appear

(12) This Bulletin, **10** (1935), 220.
(13) Dadieu, Pongratz, and Kohlrausch, *Monatsh.*, **60** (1932), 253.
(14) Kohlrausch, "Smekal-Raman-Effekt", 1931, p. 332.

constantly, while $\Delta\nu$ 616 and 1166 cm.$^{-1}$ disappear occasionally. They have concluded also that the Raman line corresponding to ξ = ca. 1040 cm.$^{-1}$ appears intensely and that corresponding to $\gamma = 1000$ disappears in the ortho-di-derivatives of benzene. We have also reported that the frequencies of $\Delta\nu$ 1000 and 615 cm.$^{-1}$ disappear in the cases of ortho-di-derivatives, such as phthalates, salicylates, and *o*-cresyl acetate(15). It is interesting that in the cases of indene, naphthalene, tetrahydro- and dihydro-naphthalene(16), the disappearance of the frequencies of 616 and 1000 cm.$^{-1}$ would indicate that these substances have the characteristic Raman spectra of the ortho-di-substitution products of benzene. The appearance of the intense line corresponding to $\Delta\nu$ 1040 cm.$^{-1}$ in tetrahydro-naphthalene, 1047 in dihydro-naphthalene, 1017 in indene, and 1026 in naphthalene indicates also the character of the ortho-di-substitution products of benzene.

In tetrahydro-acenaphthene the disappearance of $\Delta\nu$ 1000 and the appearance of $\Delta\nu$ 607, 650, 1157, 1609 and 3043 cm.$^{-1}$ may correspond to $\Delta\nu$ 615, 668, (1154), (1596), and 3036 cm.$^{-1}$ in xylenol (1 : 2 : 3)(14) and 611, 671, (1161), 1582 and 3050 cm.$^{-1}$ in xylidine (1 : 2 : 3)(14). The appearance of the intense lines corresponding to 650 in tetrahydro-acenaphthene, 654 in 1,2,3-trimethylbenzene(17), 668 in xylenol and 671 in xylidine seems to characterise the tri-(1 : 2 : 3)-substitution products of benzene.

Thus, in the case of phenyl-cyclohexane which can be considered as a mono-substitution product of benzene on one hand, and as that of cyclohexane on the other from the chemical constitution, the Raman frequencies can be classified into groups, one due to the benzene ring, viz., $\Delta\nu$ 411, 621, 839, 995, 1002, 1030, 1198, 1574–1608 cm.$^{-1}$, etc., another due to the cyclohexane ring, viz., 380, 437, 827, 862, 1048, 1155, 1262, 1349 and 1440 cm.$^{-1}$ and the rest due to the combination frequencies, such as 277, 741, 773, 894, 1082, etc. As to the frequencies above 2850 cm.$^{-1}$, it is well known that the frequencies $\Delta\nu$ 2852 and 2932 cm.$^{-1}$ are attributable to the valency frequencies of the aliphatic C–H bond and 3062 cm.$^{-1}$ to the aromatic C–H bond.

In Fig. 1 and Fig. 2, α, β, γ, ξ, δ and ε denote the frequencies associated with the benzene ring, ω_1, ω_2, ω_3, ω_4, ω_5, ω_6, ω_7, and ω_8 those associated with the cyclohexane ring. As will be obvious from the figures, some of the frequencies in the region of ca. $\Delta\nu$ 850 and 1040 cm.$^{-1}$ can be considered due to the benzene ring as well as to the cyclohexane ring.

(15) This Bulletin, **9** (1934), 87.

(16) Bonino and Cella, *Atti accad. Lincei*, **15** (1932), 572.

(17) Kohlrausch and Pongratz, *Monatsh.*, **65** (1934), 6.

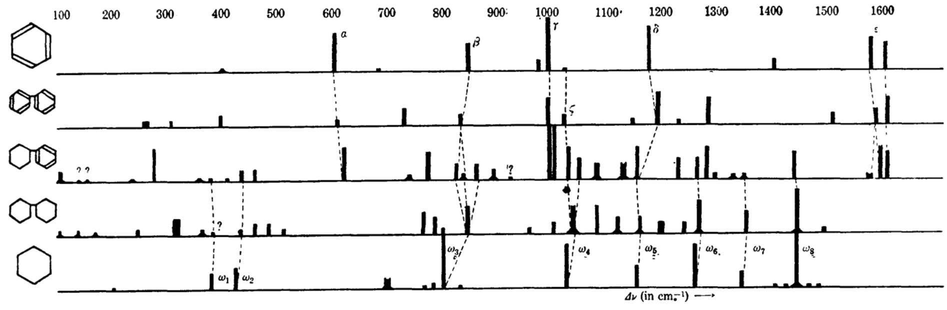


Fig. 1.

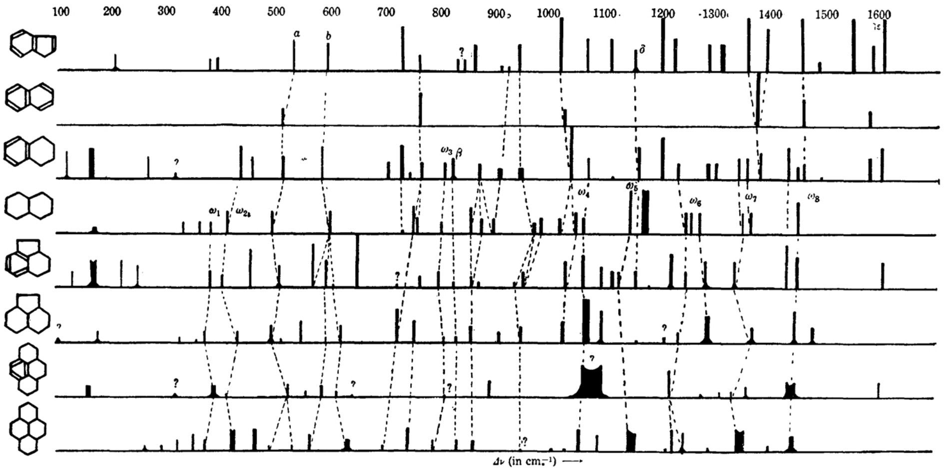


Fig. 2.

In the same way, we may consider tetrahydro-naphthalene, tetrahydro-acenaphthene and decahydro-pyrene as the substitution products of benzene as well as cyclohexane, as mentioned above. In these cases, the possible effect of the condensed ring may be the displacement or disappearance or spalting of the lines.

It is to be noted that the frequency of ca. $\Delta\nu$ 491 cm.$^{-1}$ appears in decahydro-naphthalene, decahydro-acenaphthene, and perhydro-pyrene which have the

```
             C   C
              \ /
linkage of    C—C   ,  while Δν 532 cm.⁻¹ appears in indene and ca. 514 cm.⁻¹
              / \
             C   C
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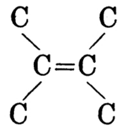
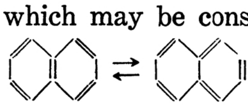
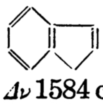
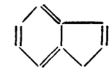
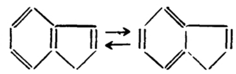
in naphthalene, tetrahydro-naphthalene and tetrahydro-acenaphthene which have a linkage of  in the ring. A line at ca. $\Delta\nu$ 590 cm.$^{-1}$ is observed also in all the condensed ring compounds, except naphthalene. The frequency of $\Delta\nu$ 1435 cm.$^{-1}$ appears in the case of dihydro-naphthalene, tetrahydro-naphthalene, tetrahydro-acenaphthene and decahydro-pyrene.

The fact that the more complicated Raman spectrum is obtained in the case of indene than that of naphthalene may be explained by the reasons that naphthalene has the higher degree of symmetry than indene and that naphthalene has been observed in solution while indene in liquid state. It is interesting that the doublet at $\Delta\nu$ 1583 and 1605 cm.$^{-1}$ appear in benzene, and 1576 and 1615 cm.$^{-1}$ in cyclohexadiene -(1, 3)[18] while only a line at $\Delta\nu$ 1577 cm.$^{-1}$ appears in naphthalene which may be considered as the resonance between the two forms, that is:  Bright Wilson[19] has explained the doublet of $\Delta\nu$ 1587 and 1605 cm.$^{-1}$ in the Raman spectrum of benzene on the basis of quantum mechanical resonance between ν_8(1587–1605) and $\nu_1(991)+\nu_6(605)$. In the case of naphthalene, the disappearance of one of the doublet in benzene, mentioned above, may be reasonable, for ν_1(991) and ν_6(605) do not occur in naphthalene. It is remarkable that, besides the frequencies of $\Delta\nu$ 1587 and 1609 cm.$^{-1}$, a very intense line corresponding to 1550 cm.$^{-1}$ appears in indene. From the fact that only the line at 1500 cm.$^{-1}$ appears in the case of cyclopentadiene[20] in place of 1494 cm.$^{-1}$ in furane[21], we may consider that the frequency of 1550 cm.$^{-1}$ in indene may correspond to that of $\Delta\nu$ 1500 cm.$^{-1}$ in cyclopentadiene, and the existence of the other two lines, viz., $\Delta\nu$ 1587 and 1609 cm.$^{-1}$, is associated with the benzene ring. Consequently, the molecule of indene can be considered as the derivatives of benzene as well as of cyclopentadiene, which corresponds to the normal expression of the chemical formula:  . It has to be assumed, however, in this case that the frequencies of $\Delta\nu$ 1584 cm.$^{-1}$ which is associated with the benzene ring is little influenced by the condensed ring as in the case of naphthalene and tetrahydro-naphthalene, while that of $\Delta\nu$ 1500 cm.$^{-1}$ which is associated with the cyclopentadiene ring is considerably influenced by the condensed ring. Since the frequencies of $\Delta\nu$ 1585 and 1615 cm.$^{-1}$ have been

(18) J. W. Murray, *J. Chem. Physics*, **3** (1935), 59.
(19) E. Bright Wilson, *Phys. Rev.*, **46** (1934), 146.
(20) R. Truchet and J. Chapron, *Compt. rend.*, **198** (1934), 1934.
(21) L. Médard, *Bull. soc. chim.*, (5), **1** (1934), 934.

also observed in cyclopentene[22], it seems reasonable to consider the molecule of indene as a derivative of benzene as well as of cyclopentene, that is, the existence of the form of  can also be considered. Consequently, the existence of the two forms is more probable, that is , as in the case of naphthalene.

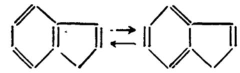
Summary.

1. The Raman spectra of the following substances have been measured: benzene, cyclohexane, phenyl-cyclohexane, di-cyclohexyl, indene, naphthalene, tetrahydro-naphthalene, decahydro-naphthalene, tetrahydro-acenaphthene, decahydro-acenaphthene, decahydro-pyrene, and perhydro-pyrene.

2. A complete Raman spectrum of cyclohexane has been obtained.

3. Considering phenyl-cyclohexane, tetrahydro-naphthalene, tetrahydro-acenaphthene, and decahydro-pyrene as the substitution products of benzene as well as of cyclohexane, the Raman frequencies of these substances have been classified into three groups, i. e., the first due to the benzene ring, the second due to the cyclohexane ring, and the third due to the combination of the two.

4. The disappearance of $\Delta\nu$ 616 and 1000 cm.$^{-1}$ in the di-derivatives (ortho) of benzene has been confirmed even in the case of the condensed ring compounds, such as indene, naphthalene, and tetrahydro-naphthalene.

5. The oscillation of the two forms of indene, i. e. , has been explained.

In conclusion, the authors wish to express their thanks to Dr. Kageyama for his supply of the samples. The authors express their indebtedness to Ass. Prof. T. Nozoe for his kind advices. A part of expenses of this experiment was defrayed from a grant given by the Nippon Gakujutsu-Shinkokwai, to which thanks are due.

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(22) L. Piaux, *Compt. rend.*, **198** (1934), 1496.